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(54) PRODUCTION OF (METH)ACRYLIC POLYMER HAVING TERMINAL FUNCTIONAL GROUP

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a process for producing a (meth)acrylic polymer having a large amount of terminal crosslinkable functional groups such as alkenyl or crosslinkable silyl groups and to provide a curable composition comprising the same.
SOLUTION: An initiator comprising an organic halide or halogenated sulfonyl compound and a catalyst comprising a metal complex having as the central metal an element belonging to Group 8, 9, 10, or 11 or the Periodic Table are used for polymerization to obtain a (meth)acrylic polymer having a terminal structure represented by the formula -CH2-C(R1)(CO2R2)(X) (R1 is hydrogen or methyl; R2 is a 1-20C alkyl, aryl, or aralykyl; and X is chloride, bromine, or iodine). The halogen atoms of the polymer are replaced with substituents each having an alkenyl or crosslinkable silyl group to obtain the target polymer.

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CLAIMS

[Claim(s)]
[Claim 1]An organic halogenated compound or a sulfonyl halide compound An initiator, the 8th fellows of the periodic table, . Are obtained by a polymerization method using a metal complex which uses nine fellows, ten fellows, or 11 group elements as a central metal as a catalyst. A manufacturing method of an acrylic polymer which has an alkenyl group at the end (meta) changing into an alkenyl group content substituent halogan of an acrylic polymer which haa terminal structuras shown by the genaral formula 1 (mata).

$-CH_2-C(R^1)(CO_2R^2)(X)$ (1)

(As for hydrogen or a methyl group, and R^2, in inside of formula, and R^1, an alkyl group of 1-20, an aryl group or an aralkyl group, and X are [a carbon number] chlorine, bromine, or iodina)
[Claim 2]An organic halogenated compound or a sulfonyl halide compound An initiator, the 8th fellows of the periodic table. An acrylic polymer which has terminal structures which show nine fellows, ten fellows, or 11 group elements by the general formula 1 with a polymerization method using a metal complex used as a central metal as a catalyst (meta) is manufactured. The manufacturing method according to claim 1 making a compound having an alkenyl group of polymerization nature, and other at least one alkenyl group react.
[Claim 3]The manufacturing method according to claim 2 which is a compound in which a compound having an alkenyl group of polymerization nature and other at least one alkenyl group is shown by the general formula 2.

$H_2C=C(R^3)-R^4-R^5-C(R^6)=CH_2$ (2)

(As for R^3 and R^6, -C(O) O- (estar group) or o-, m-, p-phenylene group, and R^5 may include one or more ether bonds among a formula by a divalent organio group of direct coupling or the carbon numbars 1-20, aa for hydrogan or mathyl, and R^4.)
[Claim 4]The manufacturing method according to claim 1 making an organic metallic compound which has an alkenyl group react to an acrylic polymer which has terminal structures shown by the general formula 1 (meta).
[Claim 5]The manufacturing method according to claim 4, wherein an organic metallic compound which has an alkenyl group is an organic tin compound shown by the general formula 3.

$H_2C=C(R^7)C(R^8)(R^9)Sn(R^{10})_3$ (3)

among a formula, R^7, R^8, and R^9 may be mutually the same at hydrogen or an alkyl group of the carbon numbers 1-10, an aryl group, or an aralkyl group, or may differ from each other. R^{10} is an alkyl group of the carbon numbers 1-10, an aryl group, or an aralkyl group.
[Claim 6]The manufacturing method according to claim 1 to 5, wherein an organic halogenated compound which is an initiator, or a sulfonyl halide compound is a halogenide which has an alkenyl group.
[Claim 7]The manufacturing method according to claim 6 which is a compound in which a halogenide which has an alkenyl group is shown by the general formula 4 or 5.

$R^{11}R^{12}C(X)-R^{13}-R^{14}-C(R^1)=CH_2$ (4)

inside of formula, and R^1 — hydrogen or a methyl group, R^{11}, and R^{12} — hydrogen. Or a univalent alkyl group of the carbon numbers 1-20, an aryl group, an aralkyl group or a thing mutually connected

in the other end, and R^{13}, -X in which C(O) O- (aster group), -C(O)- (keto group) or o-, m-, p-phanylane group, and R^{14} may include one or more ether bonds by a divalent organic group of diract coupling or the carbon numbera 1-20 is chlorine, bromine, or iodine.

$H_2C=C(R^1)-R^{14}-C(R^{11})(X)-R^{15}-R^{12}$ (5)

(a formula — inside -- R -- -- one -- -- R -- — 11 — -- R -- — 12 — — R -- — 14 -- — X -- the above — the same — R -- — 15 — -- direct coupling - C — (— O --) — O - (ester group) - C(O)- (keto group) or o-, m-, and p-phenylene group)
[Claim 8]An acrylic polymer which has the structure which is shown to one end by alkenyl group and shown in other ends by the general formula 1 by a method of claim 6 or 7 (meta) is manufactured. A manufacturing method of an acrylic polymer which has an alkenyl group at the end (meta) characterized by carrying out coupling of the halogen ends using a compound which can furthermore replace halogen of the general formula 1, and which has a total of two or more same or different functional groups.
[Claim 9]The manufacturing method according to claim 8 performing a coupling reaction of the halogen ends of the general formula 1 using a compound chosen from a group which consists of polyol, polyamine, polycarboxylic acid, polythiol and those salts, and an alkaline metal sulfide.
[Claim 10](A) an acryllo polymer which has an alkenyl group at the end obtained by one method of claims 1-9 (meta-), and a hardanability constituent containing (B) hydrosilyl group content compound.

[Claim 11](A) The hardenability constituent according to claim 10 which has a molecular weight of an acrylic polymer which has an alkenyl group at the end of an ingredient (meta) in the range of 500-50000.
[Claim 12]An organic halogenated compound or a sulfonyl halide compound An initiator, the 8th fellows of the periodic table, . Are obtained by a polymerization method using a metal complex which uses nine fellows, ten fellows, or 11 group elements as a central metal as a catalyst. A manufacturing method of an acrylic polymer which has crosslinkable silyl groups at the end (meta) changing into a crosslinkable-silyl-groups content substituent halogen of an acrylic polymer which has terminal structures shown by the general formula 1 (meta).
[Claim 13]An organic halogenated compound or a sulfonyl halide compound An initiator, the 8th fellows of the periodic table. An acrylic polymer in which nine fellows, ten fellows, or 11 group elements are shown by the general formula 1 with a polymerization method using a metal complex used as a central metal as a catalyst (meta) is manufactured. The manufacturing method according to claim 12 making a compound having an alkenyl group and crosslinkable silyl groups of polymerization nature react.
[Claim 14]The manufacturing method acoording to olaim 13 whose compound having an alkenyl group and crosslinkable silyl groups of polymerization nature ia a compound shown by the general formule 6.

$H_2C=C(R^3)-R^4-R^5-[Si(R^{16})_{2-b}(Y)_bO]-_m-Si(R^{17})_{3-a}(Y)_a$ (6)

(R^3, R^4, and R^5 among a formula) R^3 in the general formula 2, R^4, and R^5 -- the same -- R^{16} and R^{17}, All An alkyl group of the carbon numbers 1-20, an aryl group, an aralkyl group. Or $(R')_3SiO$ - (R' is a univalent hydrocarbon group of the carbon numbers 1-20, and) three R' being the same and differing -- **** -- when the Tori ORGANO siloxy group shown is shown and R^{16} or two or more R^{17} exist, they may be the same and may differ. When Y shows a hydroxyl group or a hydrolytic basis and two or more Y exists, they may be the same and may differ.a shows 0, 1, 2, or 3, and b shows 0, 1, or 2. m is an integer of 0-19. However, it shall satisfy that it is a+mb>=1.
[Claim 15]The manufacturing method according to claim 12 to 14 which is an organic halogenated compound which is an initiator, or a halogenide in which a sulfonyl halide compound has crosslinkable silyl groups.
[Claim 16]The manufacturing method aocording to claim 15 which is a compound in which an organic halogenated compound which has crosslinkable silyl groups is shown by tha general formule 7 or 8.

$R^{11}R^{12}C(X)-R^{-13}-R^{14}-C(H)(R^1)CH_2-[Si(R^{16})_{2-b}(Y)_bO]_m-Si(R^{17})_{3-a}(Y)_a$ (7)

(The inside of a formula, R^1, R^{11}, R^{12}, R^{13}, R^{14}, R^{16}, R^{17}, a, b, m, X, and Y are the aame aa the above)

$(R^{17})_{3-a}(Y)_a Si-[OSi(R^{16})_{2-b}(Y)_b]_m-CH_2-C(H)(R^1)-R^{14}-C(R^{11})(X)-R^{15}-R^{12}$ (8)

(The inside of a formula, R^1, R^{11}, R^{12}, R^{14}, R^{15}, R^{16}, R^{17}, a, b, m, X, and Y are the same as the above)

[Claim 17]An acrylic polymer which has the structure which is shown to one end by crosslinkable silyl groups, and is shown in other ends by the general formula 1 by a method of claim 15 or 16 (meta) is manufactured, A manufacturing method of an acrylic polymer which has crosslinkable silyl groups at the end (meta) characterized by carrying out coupling of the halogen ends using a compound which can furthermore replace halogen of the general formula 1, and which has a total of two or more same or different functional groups.

[Claim 18]The manufacturing method according to claim 17 performing a coupling reaction of the halogen ends of the general formula 1 using a compound chosen from a group which consists of polyol, polyamine, polycarboxylic acid, polythiol and those salts, and an alkaline metal sulfide.

[Claim 19]A manufacturing method of an acrylic polymer which has crosslinkable silyl groups at the end (meta) making hydrosilane which has crosslinkable silyl groups add to an acrylic polymer which has an alkenyl group at the end obtained by one method of claims 1-9 (meta).

[Claim 20]A hardenability constituent which uses as the main ingredients an acrylic polymer which is obtained by one of methods according to claim 12 to 19, and which has crosslinkable silyl groups at the end (meta).

[Claim 21]The hardenability constituent according to claim 20 which has a molecular weight of an acrylic polymer which has crosslinkable silyl groups at the end (meta) in the range of 500-50000.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the hardenability constituent which used for the end the manufacturing method of a functional group and the acrylic polymer which specifically has an alkenyl group or crosslinkable silyl groups (meta), and this polymer.
[0002]
[Description of the Prior Art]The polymer which has a functional group at the end constructs a bridge by combining with a the very thing independent or a suitable hardening agent, and giving the hardened material which was excellent in heat resistance, endurance, etc. is known. The polymers which have an alkenyl group or crosslinkable silyl groups at the end especially are those examples of representation. The polymer which has an alkenyl group at the end carries out bridge construction hardening using a hydrosilyl group content compound as a hardening agent, or by using the photoreaction. The polymer which has crosslinkable silyl groups at the end gives a hardened material by absorbing hygroscopic surface moisture under existence of a suitable condensation catalyst.
[0003]As a principal chain skeleton of the polymer which it has at the end, such an alkenyl group or crosslinkable silyl groups, Polyether system polymers, such as polyethylene oxide, polypropylene oxide, polytetramethylene oxide, Hydrocarbon system polymers, such as polybutadiene, polyisoprene, polychloroprene, polyisobutylenes, or those hydrogenation things, Polyester system polymers, such as polyethylene terephthalate, polybutylene terephthalate, and polycaprolactone, etc. are illustrated, and it is used for various uses based on a principal chain skeleton and bridge construction form.
[0004]
[Problem(s) to be Solved by the Invention]What has a functional group at the end with the polymer of a vinyl system obtained by a radical polymerization by one side of the polymer which was illustrated above, and which is obtained by ionic polymerization or condensation polymerization has hardly been put in practical use yet. Also in a vinyl system polymer, an acrylic (meta) polymer, It has the characteristics which are not obtained in an above-mentioned polyether system polymer, hydrocarbon system polymer, or polyester system polymer, such as high weatherability and transparency, and what has an alkenyl group and crosslinkable silyl groups in a side chain is used for the high weatherability paint etc.
[0005]If the acrylic polymer which has an alkenyl group or crosslinkable silyl groups in molecular chain terminals (meta) can be obtained by a simple method, the hardened material which excelled [side chain] in hardened material physical properties as compared with what has a cross-linking group can be obtained. Therefore, although the manufacturing method has been examined by the researcher of the former many, it is not easy to manufacture them industrially.
[0006]. Use alkenyl group content disulfide for JP,5-255415,A as a chain transfer agent. The synthetic method of the acrylic polymer which has an alkenyl group in both ends (meta) again to JP,5-262808,A. Although the acrylic polymer which has hydroxyl in both ends (meta) is compounded using the disulfide which has hydroxyl and the synthetic method of the acrylic polymer which has an alkenyl group in both ends further using the reactivity of hydroxyl (meta) is indicated, It is not easy to introduce an alkenyl group into both ends certainly by these methods. On the other hand to JP,59-168014,A, the manufacturing method of the acrylic polymer which has crosslinkable silyl groups as a chain transfer agent in the both ends using the disulfide compound which has crosslinkable silyl groups (meta), Although the manufacturing method of the acrylic polymer which has crosslinkable silyl

groups in both ends (meta) by using for JP,61-133201,A the hydrosilane which has crosslinkable silyl groups, and halogenation Silang is indicated, In these methods, it is difficult to introduce crosslinkable silyl groups into both ends certainly, and the hardened material which has the satisfactory characteristic cannot be obtained. In order to introduce a functional group into an end certainly, a chain transfer agent must be used in large quantities, and it is a manufacturing process top problem.
[0007]Therefore, let it be SUBJECT to provide the manufacturing method of the acrylic polymer which has an alkenyl group or crosslinkable silyl groups by a high ratio at the end as compared with the conventional method (meta), and the hardenability constituent using them in this invention.
[0008]
[Means for Solving the Problem]An acrylic polymer which has an alkenyl group at the end among aforementioned problems (meta), An organic halogenated compound or a sulfonyl halide compound An initiator, the 8th fellows of the periodic table, It is obtained by changing into an alkenyl group content substituent halogen of an acrylic polymer which has terminal structures which show by the general formula 1 (meta) obtained by a polymerization method using a metal complex which uses nine fellows, ten fellows, or 11 group elements as a central metal as a catalyst.
$-CH_2-C(R^1)(CO_2R^2)(X)$ (1)
(As for hydrogen or a methyl group, and R^2, in inside of formula, and R^1, an alkyl group of 1-20, an aryl group or an aralkyl group, and X are [a carbon number] chlorine, bromine, or iodine)
As an example of such a manufacturing method, an organic halogenated compound or a sulfonyl halide compound An initiator, An acrylic polymer which has the structure which shows the 8th fellows of the periodic table, nine fellows, ten fellows, or 11 group elements by the general formula 1 with a polymerization method using a metal complex used as a central metal as a catalyst (meta) is manufactured, A method of making an organic metallic compound which has an alkenyl group react to an acrylic polymer which has a method to which a compound having an alkenyl group of polymerization nature and other at least one alkenyl group is made to react, or terminal structures shown by the general formula 1 (meta), etc. are mentioned. A halogenide which has an alkenyl group, or a sulfonyl halide compound is used as an initiator, An acrylic polymer which has an alkenyl group at the end (meta) can be obtained also by manufacturing an acrylic polymer which has an alkenyl group in one end and has the structure of the formula 1 at other ends (meta), and changing halogen of the end into an alkenyl group content substituent.
[0009]An acrylic polymer which is obtained by such a method and which has an alkenyl group at the end (meta) is used for an acrylic polymer which has an alkenyl group at the (A) end (meta), and a hardenability constituent containing (B) hydrosilyl group content compound. An acrylic polymer which has crosslinkable silyl groups at the end (meta), An organic halogenated compound or a sulfonyl halide compound An initiator, the 8th fellows of the periodic table, It can manufacture by changing into a crosslinkable-silyl-groups content substituent halogen of an acrylic polymer which has terminal structures which show by the general formula 1 (meta) obtained by a polymerization method using a metal complex which uses nine fellows, ten fellows, or 11 group elements as a central metal as a catalyst. As an example of such a manufacturing method, an organic halogenated compound or a sulfonyl halide compound An initiator, An acrylic polymer which has terminal structures which show the 8th fellows of the periodic table, nine fellows, ten fellows, or 11 group elements by the general formula 1 with a polymerization method using a metal complex used as a central metal as a catalyst (meta) is manufactured, A method to which a compound having an alkenyl group and crosslinkable silyl groups of polymerization nature is made to react is mentioned. A halogenide which has crosslinkable silyl groups is used as an initiator, It can obtain also by manufacturing an acrylic polymer which has crosslinkable silyl groups in one end, and has the structure shown in other ends by the formula 1 (meta), and changing halogen of the end into a crosslinkable-silyl-groups content substituent further.
[0010]An acrylic polymer which has crosslinkable silyl groups at the end (meta) can be manufactured also by making hydrosilane which has crosslinkable silyl groups add to an acrylic polymer which has an alkenyl group at the end (meta). Thus, an acrylic polymer which has crosslinkable silyl groups at the end obtained (meta) can be used as a hardenability constituent.
[0011]It also has the feature that an acrylic polymer which has a functional group of cross-linking at the end obtained by this invention (meta) has narrow molecular weight distribution.
[0012]

[Embodiment of the Invention]First, the manufacturing method of the acrylic polymer which has an alkenyl group at the end (meta), An organic halogenated compound or a sulfonyl halide compound An initiator, the 8th fellows of the periodic table, The halogen of the acrylic polymer which has terminal structures which show by the general formula 1 (meta) obtained by the polymerization method using the metal complex which uses nine fellows, ten fellows, or 11 group elements as a central metal as a catalyst is changed into an alkenyl group content substituent.

$-CH_2-C(R^1)(CO_2R^2)(X)$ (1)

(As for hydrogen or a methyl group, and R^2, in inside of formula, and R^1, the alkyl group of 1-20, an aryl group or an aralkyl group, and X are [a carbon number] chlorine, bromine, or iodine)
The method of using a carbon tetrachloride, carbon tetrabromide, a methylene chloride, a methylene bromide, etc. for an end in the polymerization which uses a halogenide as a chain transfer agent (TEROGEN) as a manufacturing method of the acrylic polymer which has halogen (meta) is used. However, it is difficult to introduce halogen into both ends certainly by this method.
[0013]If the living radical polymerization studied energetically these days is used to this method, halogen is introduced into an end by a high ratio (Matyjaszewski et al. [for example,].) J. Refer to Am.Chem.Soc.1995, 117 and 5614, Macromolecules 1995, 28, and 7901, Science 1996, 272, and 866 or Sawamoto et al., and Macromolecules 1995, 28, and 1721. Though these methods are radical polymerizationa, a polymerization advances in living, the narrow (Mw/Mn=1.1-1.5) polymer of molecular weight distribution is obtained, and a molecular weight can be freely controlled by the preparation ratio of a monomer and an initiator.
[0014]The organic halogenated compound which has an organic halogenated compound and a carbon-halogen bond with especially high reactivity in this living radical polymerization. (For example, the ester compound which has halogen in an alpha position and the compound which has halogen in a benzylic position), or a sulfonyl halide compound is used as an initiator. As a catalyst, the metal complex which uses the 8th fellows of the periodic table, nine fellows, ten fellows, or 11 group elements as a central metal is used. As a metal kind, univalent copper, a divalent ruthenium, and divalent iron are especially preferred. If it illustrates concretely, they will be a cuprous chloride, the first copper of bromination, a cuprous iodide, a cuprous cyanide, copper I oxide, the first copper of acetic acid, the first copper of perchloric acid, etc. When using a copper compound, in order to improve catalytic activity, ligands, such as a 2,2'-bipyridyl and its derivative, a 1,10-phenanthroline, and its derivative, are added. The tristriphenyl phosphine complex ($RuCl_2(PPh_3)_3$) of ruthenium chloride of bivalence is also preferred as a catalyst. when using this catalyst, in order to improve that activity -- doria -- aluminium compounds, such as RUKOKI sial minium, are added. The tristriphenyl phosphine complex ($FeCl_2(PPh_3)_3$) of the ferric chloride of bivalence is also preferred as a catalyst.
[0015]In order to obtain the acrylic (meta) polymer of cross-linking using this polymerizing method, the organic halogenated compound which has the two or more starting points, or a sulfonyl halide compound is used as an initiator. If it illustrates concretely, o-, m-, $p-XCH_2-C_6H_4-CH_2X$, o-, m-, $p-CH_3C(H)(X)-C_6H_4-C(H)(X)CH_3$, o-, m-, $p-(CH_3)_2C(X)-C_6H_4-C(X)(CH_3)_2$ (however, inside of upper chemical formula, and C_6H_4 a phenylene group and X chlorine, bromine, or iodine),
$RO_2C-C(H)(X)-(CH_2)_n-C(H)(X)-CO_2R$, $RO_2C-C(CH_3)(X)-(CH_2)_n-C(CH_3)(X)-CO_2R$, $RC(O)-C(H)(X)-(CH_2)_n-C(H)(X)-C(O)R$, $RC(O)-C(CH_3)(X)-(CH_2)_n-C(CH_3)(X)-C(O)R$ (as for the alkyl group of the carbon numbers 1-20, an aryl group or an aralkyl group, and n, in the inside of a formula, and R, the integer of 0-20 and X are chlorine, bromine, or iodine),
$XCH_2C(O)CH_2X$ and $CH_3C(H)(X)-C(O)C(H)(X)CH_3$, $(CH_3)_2C(X)C(O)C(X)(CH_3)_2$, $C_6H_5C(H)(X)-(CH_2)_n-C(H)(X)C_6H_5$ (as for the inside of the upper formula, and X, chlorine, bromine or iodine, and n are the integers of 0-20),
$XCH_2CO_2-(CH_2)_n-OCOCH_2X$, $CH_3C(H)(X)CO_2-(CH_2)_n-OCOC(H)(X)CH_3$, $(CH_3)_2C(X)CO_2-(CH_2)_n-OCOC(X)(CH_3)_2$ (as for the inside of the upper formula, and X, chlorine, bromine, iodine, and n are the integers of 0-20),
$XCH_2C(O)C(O)CH_2X$ and $CH_3C(H)(X)-C(O)C(O)C(H)(X)CH_3$, $(CH_3)_2C(X)C(O)C(O)C(X)(CH_3)_2$, o-, m-, $p-XCH_2CO_2-C_6H_4-OCOCH_2X$, o-, m-, $p-CH_3C(H)(X)CO_2-C_6H_4-OCOC(H)(X)CH_3$, o-, m-, $p-(CH_3)_2C(X)CO_2-C_6H_4-OCOC(X)(CH_3)_2$, o-, m-, $p-XSO_2-C_6H_4-SO_2X$ (the inside of the upper formula and X are chlorine, bromine, or iodine),
** is mentioned.

[0016]As an acrylic monomer used in this polymerization (meta), there are no restrictions in particular and various kinds of things can be used. If it illustrates, methyl acrylate (meta), ethyl acrylate (meta), (Meta) Acrylic acid-n-propyl, acrylic acid (meta) isopropyl, (Meta) Acrylic acid-n-butyl, isobutyl acrylate (meta), (Meta) Acrylic acid-tert-butyl, acrylic acid (meta)-n-pentyl, (Meta) Acrylic acid-n-hexyl, acrylic acid (meta) cyclohexyl, (Meta) Acrylic acid-n-heptyl, acrylic acid (meta)-n-octyl, (Meta) Acrylic acid-2-ethylhexyl, acrylic acid (meta) nonyl, (Meta) Decyl acrylate, acrylic acid (meta) dodecyl, acrylic acid (meta) phenyl, (Meta) They are acrylic acid toluyl, acrylic acid (meta) benzyl, acrylic acid (meta)-2-methoxy ethyl, acrylic acid (meta)-3-methoxy butyl, acrylic acid (meta)-2-hydroxyethyl, acrylic acid (meta)-2-hydroxypropyl, etc. Even if it uses these independently and they mix and use two or more sorts, they are not cared about. Carrying out copolymerization of other vinyl system monomers, such as styrene, alpha-methylstyrene, acrylonitrile, if needed does not interfere at all.
[0017]A polymerization can be performed in a non-solvent or various kinds of solvents. A polymerization can be performed in room temperature -200 **, and it is 50-150 ** preferably. The acrylic polymer which has an alkenyl group at the end (meta) can be obtained by changing halogen of the acrylic polymer which is obtained by the above-mentioned polymerization and which has halogen at the end (meta).
[0018]As such a method, first, the acrylic polymer which has terminal structures shown by the general formula 1 by the above-mentioned polymerization (meta) is manufactured, and the method to which the compound it has a compound and an alkenyl group of polymerization nature and other at least one alkenyl group further is made to react as the 2nd monomer is mentioned. In the above-mentioned polymerization, the polymerization end holds polymerization activity, and if a vinyl system monomer is newly added, a polymerization will advance again. Therefore, if the vinyl system monomer having the alkenyl group of polymerization nature and other at least one alkenyl group is added, A radical addition reaction occurs in a polymerization activity alkenyl group portion, other alkenyl groups remain, while it has been unreacted, and the acrylic polymer which has an alkenyl group at the end (meta) is obtained. After the 1st polymerization is completed and it isolates a polymer, it may add with a catalyst and such 2nd monomer may be made to newly react, and it may add in the middle of a polymerization (inch-situ), and it may be made to react. In the case of the latter, the monomer inversion rate of the 1st polymerization is so good that it is high, and is not less than 80% preferably. An alkenyl group will be distributed over the side chain instead of a molecular terminal as it is 80% or less, and the mechanical characteristic of a hardened material will be spoiled.
[0019]Under the present circumstances, the compound having the alkenyl group of such polymerization nature, and other at least one alkenyl group, If a quantity equal to the number of polymerization ends (it is almost equal to the number of the starting points of an initiator since it is living polymerization) is added, one alkenyl group will be theoretically introduced into all the ends at a time, but. In order to introduce an alkenyl group into a whole end certainly, specifically, it is good to use one to 5 times to the number of ends in excessive amount. If it uses more mostly than 5 times, an alkenyl group will be introduced into the end of a polymer by high density, and it is not desirable on hardened material physical properties.
[0020]Although there is no restriction in particular as a compound having the alkenyl group of polymerization nature, and other at least one alkenyl group, it is general formula $2H_2C=C(R^3)-R^4-R^5-C(R^6)=CH_2$ (2), for example.

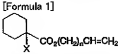
the inside of a formula, R^3, and R^6 -- hydrogen or methyl, and R^4 -C(O) O- (ester group). Or o-, m-, p-phenylene group, and R^5 may include one or more ether bonds by the divalent organic group of direct coupling or the carbon numbers 1-20. The compound shown is mentioned. As for the thing of an ester group, R^4 is [an acrylate (meta) system compound and R^4 of the thing of a phenylene group] the compounds of a styrene system. As R^5 in the general formula 2, alkylene groups, such as methylene, ethylene, and propylane, An alkylene group including ether bonds, such as aralkyl group [,

such as o-, m-, p-phenylene group, and benzyl.] and $-CH_2CH_2-O-CH_2-$ and $-O-CH_2-$, are illustrated.
[0021]H from the point that acquisition is easy also in these -- $_2C=CC[(H)] (O) O(CH_2)_n-CH=CH_2$ and H -- $_2C=C(CH_3) C(O) O(CH_2)_n-CH=CH_2$ (in each of above-mentioned formulas, n is an integer of 0-20),
$H_2C=C(H) C(O) O(CH_2)_n-O-(CH_2)_m CH=CH_2$, $H_2C=C(CH_3) C(O) O(CH_2)_n-O-(CH_2)_m CH=CH_2$ (in each of above-mentioned formulas, n is an integer of 1-20 and m is an integer of 0-20),
o-, m-, p-divinylbenzene, o-, m-, p-$H_2C=CH-C_6H_4-CH_2CH=CH_2$, o-, m-, p-$H_2C=CH-C_6H_4-CH_2-C(CH_3)=CH_2$, o-, m-, p-$H_2C=CH-C_6H_4-CH_2CH_2CH=CH_2$, o-, m-, p-$H_2C=CH-C_6H_4-OCH_2CH=CH_2$, o-, m-, p-$H_2C=CH-C_6H_4-OCH_2-C(CH_3)=CH_2$, o-, m-, p-$H_2C=CH-C_6H_4-OCH_2CH_2CH=CH_2$o-, m-, p-$H_2C=C(CH_3)-C_6H_4-C(CH_3)=CH_2$, o-, m-, p-$H_2C=C(CH_3)-C_6H_4-CH_2CH=CH_2$, o-, m-, p-$H_2C=C(CH_3)-C_6H_4-CH_2C(CH_3)=CH_2$, o-, m-, p-$H_2C=C(CH_3)-C_6H_4-CH_2CH_2CH=CH_2$, o-, m-, p-$H_2C=C(CH_3)-C_6H_4-OCH_2CH=CH_2$, o-, m-, p-$H_2C=C(CH_3)-C_6H_4-OCH_2-C(CH_3)=CH_2$, o-, m-, p-$H_2C=C(CH_3)-C_6H_4-OCH_2CH_2CH=CH_2$ (however, C_6H_4 shows a phenylene group among the above-mentioned chemical formula.)
** -- it is desirable.
[0022]If it is considered as the method of introducing an alkenyl group into an end, various kinds of organic metallic compounds which have an alkenyl group can be mada to be able to act on the end shown by the formula 1 to the polymer which has halogen, and the method of replacing halogen directly can also be used. As such an organic metallic compound, organic lithium, organic sodium, organic potassium, organic magnesium, organic tin, organic zinc, organic copper, etc. are mentioned. Organic tin and an organocopper compound are preferred at the point that react especially to halogen of the formula 1 selectively, and reactivity with a carbonyl group is low.
[0023]As an organic tin compound which has an alkenyl group, although there is no restriction in particular, the compound shown by the general formula 3 is preferred.
$H_2C=C(R^7) C(R^8) (R^9) Sn(R^{10})_3$ (3)
among the formula, R^7, R^8, and R^9 may be mutually the same at hydrogen or the alkyl group of the carbon numbers 1-10, an aryl group, or an aralkyl group, or may differ from each other. R^{10} is an alkyl group of the carbon numbers 1-10, an aryl group, or an aralkyl group.
If the example of the organic tin compound of the formula 3 is shown, allyl tributyl tin, allyl trimethyl tin, ant RUTORI (n-octyl) tin, ant RUTORI (cyclohexyl) tin, etc. will be illustrated. The alkenyl group content organic tin compound shown by the general formula 3, It may add in the middle of the polymerization of an acrylic system monomer (meta), and the acrylic polymer which has terminal structures of the general formula 1 (meta) may be mada to react anew, since it reacts to end halogen of tha general formula 1 by a radical mechanism once it isolates. In the case of the latter, a reaction advances only with heating, but in order to promote a reaction, radical initiators, such as azobisisobutyronitrile, may be added.
[0024]As an organocopper compound which has an alkenyl group, divinyl copper lithium, diaryl copper lithium, diisopropenyl copper lithium, etc. are illustrated. As a converting method to the alkenyl group of an end halogen group, It is also possible to use the method of making it react to the electrophilicity compound which makes a metal simple substance or an organic metallic compound act, metal-izes halogen to the acrylic polymer which has halogen at the end (meta), and has an alkenyl group after an appropriate time.
[0025]As a metal simple substance, alkaline-earth metals, such as alkaline metals, such as lithium, sodium, and potassium, magnesium, and calcium, aluminum, zinc, etc. are mentioned. The point that a side reaction which the metal-ized portion (eno rate anion) attacks other ester groups among these, or it transfers does not occur easily to especially zinc is preferred. As an example of an organic metallic compound, organic magnesium, such as organic lithium, organic sodium, organic potassium, and a Grignard reacting agent, organic aluminium, an organozinc compound, etc. ara mentioned. In order to make halogen metal-ize efficiently, it is preferred to use organic lithium and organic magnesium.

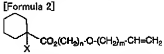
[0026]Various kinds of things can be used as an electrophilicity compound which has an alkenyl group. For example, they are an alkanyl group content compound which has a leaving group like halogen or an acetyl group, a carbonyl compound which has an alkanyl group, an isocyanate compound which has an alkenyl group, the acid halide which has an alkenyl group, etc. If the alkenyl group content compound which has a leaving group like halogen or an acetyl group among these is used, since a hetero atom will not be introduced into a main chain and tha weatherability which is the original feature of an acrylic (meta) polymer will not be lost, it is desirable.
[0027]Also in such a leaving group content alkenyl compound, for the reason reactivity is high, VCM/PVC, vinyl bromide, iodination vinyl, isopropenyl chloride, isopropenyl bromide, Iodination isopropenyl, an allyl chloride, an allyl bromide, allyl iodide, a 3-chloro-1-butene, A 3-bromo-1-butene, a 3-iodo-1-butene, a 3-chloro-2-methyl-1-propene, A 3-bromo-2-methyl-1-propene, a 3-iodo-2-methyl-1-propene, Allyl acetate, a 3-acetoxy 1-butene, a 3-acetoxy 2-methyl-1-propene, Chloridation-4-vinylbenzyl and-4-allylbenzyl chloride, bromination-4-vinylbenzyl, and-4-allylbenzyl bromide is preferred, and an allyl chloride, an allyl bromide, allyl iodide, and especially allyl acetate are preferred at the point that acquisition is still easier.
[0028]To halogen of the end of the formula 1, make a metal simple substance or an organic metallic compound act, and it metal-izes, In the manufacturing method of the acrylic polymer which has an alkanyl group at tha end (meta) making an alkenyl group content electrophilicity compound react furthermore, The combination of a daairabla reacting agant is using the above alkanyl group content compounds which have a leaving group as an electrophilicity compound, using zinc as metal. In order to advanca this reaction more smoothly, various kinds of catalysts can be usad. as such a catalyst -- the copper compound (for example, a copper chloride.) of monovalance A copper bromide, the copper compound (for example, copper acetylacetonato) of bivalence, zerovalent Ni compounds. They are (for example, tetrakis triphenyl phosphine nickel:nickel$(PPh_3)_4$), zerovalent Pd compound (for example, tetrakistriphenyl phosphinepalladium-d$(PPh_3)_4$), etc.
[0029]As a method of introducing an alkenyl group into an end, the end of the acrylic polymer which has halogen at the end as shown in the general formula 1 (meta) is further changed into a hydroxyl content substituent, and the method of using the reactivity of hydroxyl for after an appropriate time is mentioned. Various kinds of reactions can be used as a method of changing an end into a hydroxyl content substituent. For example, the acrylic polymer which has an end shown by the general formula 1 by the above-mentioned polymerizing method (meta) is manufactured, A method to which the compound it furthermore has a compound, and the alkenyl group and hydroxyl group of polymerization nature is made to react as the 2nd monomer, Aa opposed to the acrylic polymer which has a halogen end shown by the general formula 1 (meta), Make a metal simple substance or an organic metallic compound act, and halogen is metal-ized, They are the method of making it react to carbonyl compounds, such as aldehyde or ketone, the way alkali metal hydroxide like sodium hydroxide or a potassium hydrate raplaces halogen directly, the way polyalcohol replaces halogen, etc.
[0030]In addition to this as a method of introducing hydroxyl into an end, the halogenide which has a hydroxyl group by polymerization using the metal complex which uses an initiator, the 8th fellows of the periodic table, nine fellows, ten fellows, or 11 group elements as a central metal as a catalyst. The acrylic polymer which has halogen which has a hydroxyl group in one end and Is shown in other ends by the formula 1 (meta) is manufactured, After an appropriate time, the method of changing into a hydroxyl group content substituent by the method which mentioned the halogen end above, and the method of carrying out coupling of the halogen ends using the compound which has a total of two or more same or different functional groups that can replace these halogen further are mentioned.
[0031]Thus, as a method of introducing an alkenyl group into the acrylic polymer which has a hydroxyl group at the obtained end (meta), For example, a method on which a base like an alkenyl group content halogenide like an allyl chloride and sodium methoxide is made to act, A method on which alkenyl group content isocyanate compounds, such as an allylisocyanate, are made to act, (Meta) The method of making alkenyl group content acid halide like acrylic acidchloride reacting under existence of bases, such as pyridine, the method of making alkanyl group content carboxylic acid like acrylic acid (meta) react undar existence of a dehydration condensation catalyst, etc. are mentioned.
[0032]In the manufacturing method of the acrylic polymer using the metal complex which uses an initiator, the 8th fellows of the pariodic table, nine fellows, ten fellows, or 11 group elements as a central metal for an organic halogenated compound or a sulfonyl halida compound as a catalyst

(meta). If the organic halogenated compound which has an alkenyl group, or a sulfonyl halide compound is used as an initiator, the acrylic polymer which has an alkenyl group in an initiation terminal and in which a stop end has the structure of the formula 1 (meta) will be obtained. Thus, if halogen of the stop end of the polymer obtained is changed into an alkenyl group content substituent, the acrylic polymer which has an alkenyl group in both ends (meta) can be obtained.
[0033]Although there is no restriction in particular as an organic halogenated compound which has an alkenyl group, what has the structure shown in the general formula 4, for example is illustrated.
$R^{11}R^{12}C(X)-R^{13}-R^{14}-C(R^1)=CH_2$ (4)

inside of formula, and R^1 — hydrogen or a methyl group, R^{11}, and R^{12} — hydrogen. Or the univalent alkyl group of the carbon numbers 1-20, an aryl group, an aralkyl or the thing mutually connected in the other end, and R^{13}, -X in which C(O) O- (ester group), -C(O)- (keto group) or o-, m-, p-phenylene group, and R^{14} may include one or more ether bonds by the divalent organic group of direct coupling or the carbon numbers 1-20 is chlorine, bromine, or iodine.
The carbon which halogen has combined has combined with the carbonyl group or the phenyl group, a carbon-halogen bond is activated, and a polymerization starts these compounds.
[0034]As an example of substituent R^{11} and R^{12}, hydrogen, a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl group, a pentyl group, a hexyl group, etc. are mentioned. In the other end, may connect R^{11} and R^{12}, they may form the annular skeleton, and, in such a case, $-R^{11}-R^{12}-$ for example, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2CH_2-$, etc. are illustrated.
[0035]As an example of an organic halogenated compound shown by the general formula 4 of having an alkenyl group, $XCH_2C(O)$ CC[$O(CH_2)_nCH=CH_2$ and H_3] (H) (X) — C(O) $O(CH_2)_nCH=CH_2$, $(H_3C)_2C(X)$ — C(O) $O(CH_2)_nCH=CH_2$ and CH_3CH_2C (H) (X) — C(O) $O(CH_2)_nCH=CH_2$. [0036]
[Formula 1]



[0037](In each of above-mentioned formulas, as for X, chlorine, bromine or iodine, and n are the integers of 0-20)
XCH_2C (O) $O(CH_2)_nO(CH_2)_mCH=CH_2$, $H_3CC(H)$ (X)C(O) $O(CH_2)_nO(CH_2)_mCH=CH_2$, $(H_3C)_2C(X)$ — C(O) $O(CH_2)_nO(CH_2)_mCH=CH_2$ and CH_3CH_2C (H) (X) — C(O) $O(CH_2)_nO(CH_2)_mCH=CH_2$. [0038]
[Formula 2]



[0039](As for chlorine, bromine or iodine, and n, in X, in each of above-mentioned formulas, the integer of 1-20 and m are the integers of 0-20)
o,m,p-$XCH_2-C_6H_4-(CH_2)_n-CH=CH_2$, o,m,p-$CH_3C(H)$ (X)$-C_6H_4-(CH_2)_n-CH=CH_2$, O,m,p-$CH_3CH_2C(H)$ (X)$-C_6H_4-(CH_2)_n-CH=CH_2$ (in each of above-mentioned formulas, as for X, chlorine, bromine or iodine, and n are the integers of 0-20)
o,m,p-$XCH_2-C_6H_4-(CH_2)_n-O-(CH_2)_m-CH=CH_2$, o,m,p-$CH_3C(H)$ (X)$-C_6H_4-(CH_2)_n-O-(CH_2)_m-CH=CH_2$, O,m,p-$CH_3CH_2C(H)$ (X)$-C_6H_4-(CH_2)_n-O-(CH_2)_mCH=CH_2$ (as for chlorine, bromine or iodine, and n, in X, in each of above-mentioned formulas, an integer of 1-20 and m are the integers of 0-20)
o,m,p-$XCH_2-C_6H_4-O-(CH_2)_n-CH=CH_2$, o,m,p-$CH_3C(H)$ (X)$-C_6H_4-O-(CH_2)_n-CH=CH_2$, O,m,p-$CH_3CH_2C(H)$ (X)$-C_6H_4-O-(CH_2)_n-CH=CH_2$ (in each of above-mentioned formulas, as for X, chlorine, bromine or iodine, and n are the integers of 0-20),

o,m,p-$XCH_2-C_6H_4-O-(CH_2)_n-O-(CH_2)_m-CH=CH_2$, o,m,p-$CH_3C(H)$ (X)$-C_6H_4-O-(CH_2)_n-O-(CH_2)_m-CH=CH_2$, O,m,p-$CH_3CH_2C(H)$ (X)$-C_6H_4-O-(CH_2)_n-O-(CH_2)_m-CH=CH_2$ (as for chlorine, bromine or iodine, and n, in X, in each of above-mentioned formulas, an integer of 1-20 and m are the integers of 0-20),
A compound further shown by the general formula 5 as an organic halogenated compound which has an alkenyl group is mentioned.
$H_2C=C(R^1)-R^{14}-C(R^{11})$ (X)$-R^{15}-R^{12}$ (5)
(a formula — inside — R — one — R — 11 — R — 12 — R — 14 — X — the above — the same — R — 15 — direct coupling - C — (— O —) — O - (ester group) - C(O)- (keto group) or o-, m-, and p-phenylene group are expressed)
Although R^{14} is a divalent organic group (one or more ether bonds may be included) of direct coupling or the carbon numbers 1-20, when it is direct coupling, a vinyl group has combined with carbon which has combined halogen, and it is an allyl halide ghost. In this case, since a carbon-halogen bond is activated by contiguity vinyl group, there may not necessarily be any necessity of having a C(O) O basis, a phenylene group, etc. as R^{15}, and it may be direct coupling. When R^{14} is not direct coupling, in order to activate a carbon-halogen bond, as R^{15}, a C(O) O basis, C (O) basis, and a phenylene group are preferred. If a compound of the formula 5 is illustrated concretely, $CH_2=CHCH_2X$, $CH_2=C(CH_3)CH_2X$, $CH_2=CHC(H)(X)CH_3$, $CH_2=C(CH_3)C(H)(X)CH_3$, $CH_2=CHC(X)(CH_3)_2$, $CH_2=CHC(H)(X)C_2H_5$, $CH_2=CHC(H)(X)CH(CH_3)_2$, $CH_2=CHC(H)(X)C_6H_5$ and $CH_2=CHC(H)(X)CH_2C_6H_5$, $CH_2=CHCH_2C(H)(X)-CO_2R$, $CH_2=CH(CH_2)_2C(H)(X)-CO_2R$, $CH_2=CH(CH_2)_3C(H)(X)-CO_2R$, $CH_2=CH(CH_2)_8C(H)(X)-CO_2R$, $CH_2=CHCH_2C(H)(X)-C_6H_5$, $CH_2=CH(CH_2)_2C(H)(X)-C_6H_5$, $CH_2=CH(CH_2)_3C(H)(X)-C_6H_5$ (in each of above-mentioned formulas — X — chlorine, bromine or iodine, and R — an alkyl group of the carbon numbers 1-20.), An aryl group, an aralkyl group
** can be mentioned.
[0040]If an example of a sulfonyl halide compound of having an alkenyl group is given, o-, m-, p-$CH_2=CH-(CH_2)_n-C_6H_4-SO_2X$, o-, m-, p-$CH_2=CH-(CH_2)_n-O-C_6H_4-SO_2X$ (in each of above-mentioned formulas), As for X, chlorine, bromine or iodine, and n are the integers of 0-20.
It is by **.
[0041]An organic halogenated compound which has an alkenyl group, or a sulfonyl halide compound An initiator, If an acrylic (meta) monomer is polymerized with a polymerization method using a metal complex which uses the 8th fellows of the periodic table, nine fellows, ten fellows, or 11 group elements as a central metal as a catalyst, it will have an alkenyl group in one end, and an acrylic polymer which has the structure shown by the formula 1 (meta) will be obtained in other ends. If a containing halogen end of the formula 1 is changed into an alkenyl group content substituent, an acrylic polymer which has an alkenyl group in both ends (meta) will be obtained. It is possible to use all methods that restriction in particular does not have and had been described so far as such a converting method.
[0042]If an organic halogenated compound which has an alkenyl group, or a sulfonyl halide compound is used as an initiator, a polymer which is a halogen end where one end is shown by alkenyl group and other ends are shown by the formula 1 will be obtained, but. An acrylic polymer which has an alkenyl group at the end (meta) can be obtained also by carrying out coupling of the halogen ends using a compound which can replace halogen of the formula 1 of this polymer and which has a total of two or more same or different functional groups.
[0043]Although there is no restriction in particular as a thing which can replace end halogen shown by the formula 1 and which has a total of two or more same or different functional groups, polyol, polyamine, polycarboxylic acid, polythiol and those salts, an alkaline metal sulfide, etc. are preferred. If these compounds are illustrated concretely, ethylene glycol, a 1,2-propanediol, 1,3-propanediol, 2-methyl-1,3-propanediol, 2,2-dimethyl- 1,3-propanediol, 1,4-butanediol, 1,3-butanediol, 1,2-butanediol, 2,3-butanediol, A pinacol, 1,5-pentanediol, 1, 4-pentanediol, 2, 4-pentanediol, 1,6-hexanediol, 1, 7-heptane diol, 1,8-octanediol, 1,9-nonanediol, 1,10-Deccen diol, 1,12-dodecanediol, 1,2-cyclopentane diol, 1,3-cyclopentane diol, 1,2-cyclohexenediol, 1,3-cyclohexenediol, 1,4-cyclohexenediol, glycerol,

1,2,4-butanetriol, Catechol, resorcinol, hydroquinone, 1,2-dihydroxynaphthalene, 1,3-dihydroxynaphthalene, 1,5-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, 2,2'-biphenol, 4,4'-biphenol, bis(4-hydroxyphenyl)methane, 4,4'-isopropylidanephenol, 3,3'-(ethylane dioxy) diphenol, alpha and alpha'-dihydroxy-p-xylene, 1,1,1-tris(4-hydroxyphenyl) ethane, Pyrogallol, 1,2,4-benzenatriol, and alkali metal salt of the above-mentioned polyol compound, Ethylenediamine, 1, 3-diaminopropane, 1, 2-diaminopropana, 1,4-diaminobutane, 1,2-diamino-isobutane, 1,5-diaminopentane, 2,2-dimethyl- 1,3-propanediamine, A 1,6-hexanediamine, 1,7-heptanediamine, 1,8-octanediamine, 1,9-diaminononane, a 1,10-diaminodecane, a 1,12-diaminododecane, 4,4'-methylenebis (cyclohexylamine), 1,2-diaminocyclohexane, 1,3-diaminocyclohexane, 1,4-diaminocyclohexane, Alkali metal salt of 1,2-phenylenediamine, 1,3-phenylenediamine, 1,4-phenylenediamine, alpha, and alpha'-diamino-p-xylene and the above-mentioned polyamine compound, oxalic acid, malonic acid, methylmalonic acid, dimethylmalonic acid, succinic acid, Methylsuccinic acid, glutaric acid, adipic acid, 1,7-heptane dicarboxylic acid, 1,8-octanedicarboxylic acid, 1,9-nonanedicarboxylic acid, 1, 10-decane dicarboxylic acid, 1,11-undecane dicarboxylic acid, 1,12-dodecane dicarboxylic acid, 1,2-cyclopentane dicarboxylic acid, 1, 2-cyclohexanedicarboxylic acid, 1, 3-cyclohexanedicarboxylic acid, 1, 4-cyclohexanedicarboxylic acid, 1,3,5-cyclohexane tricarboxylic acid, phthalic acid, isophthalic acid, Terephthalic acid, 1,2,3-benzene tricarboxylic acid, 1, 2 and 4, 5-benzenetetracarboxylic acid, And alkali metal salt of the above-mentioned polycarboxylic acid, 1,2-ethanadithiol, 1,3-propanedithiol, 1,4-butanedithiol, 2,3-butanedithiol, 1,5-pentanedithiol, a 1,6-HEKISANJI thiol, 1,7-heptanedithiol, 1,8-octanedithiol, 1,9-nonanedithiol, 2-mercaptoethyl ether, p-xylene alpha, alpha' - and it reachea, [JICHIORU and] [1,2-benzene] [1,3-benzene] [1,4-benzene] They are alkali metal salt of the above-mentioned polythiol compound, a lithium sulfide, a sodium sulfide, a potassium sulfide, etc.

[0044]When using tha above-mentioned polyol, polyamine, polycarboxylic acid, and polythiol, In order to promote a substitution reaction, it is used together by basic compound and as the example, Lithium, sodium, potassium, sodium carbonate, potassium carbonate, sodium bicarbonate, sodium methoxide, a potassium methoxide, tert-butoxysodium, tert-butoxypotassium, sodium hydride, potassium hydride, etc. are mentioned.

[0045]The acrylic polymer which is obtained by various kinds of above-mentioned methods and which has an alkenyl group at the end (meta) can make this a hardenability constituent used as base resin. This hardenability constituent is an acrylic polymer which is obtained by one method of the (A) above and which has an alkenyl group at the end (meta), and a hardenability constituent containing (B) hydrosilyl group content compound.

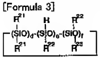
[0046](A) An acrylic polymer which has an alkenyl group at the end of an ingredient (meta) may be used independently, or two or more kinds may be mixed and it may be used. (A) Although there is no restriction in particular as a molecular weight of an ingredient, it is preferred that it is in the range of 500-50000. The original charactaristic of an acrylic (meta) polymer is it hard to ba revealed to be 500 or lesa, hyperviscosity or solubility becomes it low that it is 50000 or more dramatically, and handling becomes difficult.

[0047](B) As a hydrosilyl group content compound of an ingredient, thare is no restriction in particular and various kinds of things can be used. namely, chain polysiloxane $R^{18}{}_3SiO-[Si(R^{18})_2O]_a-$ expressed with the general formula 9 or 10 — $[Si(H)(R^{19})O]$ — $_b-[Si(R^{19})(R^{20})O]_c-SiR^{18}{}_3$ (9)

$HR^{18}{}_2SiO-[Si(R^{18})_2O]_a-[Si(H)(R^{19})O]$ — $_b-[(Si(R^{18})(R^{20})O]_c-SiR^{18}{}_2H$ (10)

Cyclosiloxane expressed with (an alkyl group of the carbon numbers 1-10 or an aralkyl group, and a show 0<=a<=100, b shows 2<=b<=100, and c shows [as for R^{18}in formula , and R^{19}] an integer of 0<=c<=100, as for an alkyl group of the carbon numbers 1-6 or a phenyl group, and R^{20}), and the general formula 11 [0048]

[Formula 3]



(11)

[0049]R^{21}in formula , and R^{22} -- the alkyl group of the carbon numbers 1-6. or -- tha alkyl group of

the carbon numbers 1-10 or an aralkyl group, and d show 0<=d<=8, e shows 2<=e<=10, and, as for a phenyl group and R^{23}, f shows the integer of 0<=f<=8 — 3<=d+e+f<=10 [and] — it is — it can use. Even if it uses these independently and they mix and usa two or mora sorts, thay are not cared about. The chain siloxane which has a phenyl group from a viewpoint of compatibility with an acrylic polymer (meta) and which is shown by the general formulas 12 and 13, and the cyclosiloxane shown by the genaral formulas 14 and 15 are preferred also in thase siloxanes.

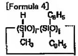
(CH_3) — $_3SiO-[Si(H)(CH_3)O]_g-[Si(C_6H_5)_2O]_h-Si(CH_3)_3$ (12)

(CH_3) — $_3SiO-[Si(H)(CH_3)O]_g-[Si(CH_3)\{CH_2C(H)(R^{24})C_6H_5\}O]_h-Si(CH_3)_3$ (13)

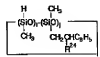
(As for hydrogen or a methyl group, and g, in R^{24}, 2<=g<=100 and h show a phenyl group among a formula, as for an integer of 0<=h<=100, and C_6H_5)

[0050]

[Formula 4]



(14)



(15)

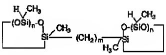
[0051](The integer and C_6H_5, as for hydrogen or a methyl group, and whose I, 2<=i<=10 and j are [inside of formula and R^{24}] 0<=j<=8 and 3<=i+j<=10 are phenyl groups)

(B) As a hardening agent which it has, at least two or more hydrosilyl groups of an ingredient further. The compound which makes carry out the addition reaction of the hydrosilyl group content compound shown in the formulas 9-15 also after a reaction to the low molecular weight compound which has two or more alkenyl groups in a molecule as some hydrosilyl groups remain, and is obtained can also be used. As a compound which has two or more alkenyl groups, various kinds of things can be used into a molecule. If it illustratas, 1,4-pentadiene, 1,5-hexadiene, 1, 6-heptadiene. Hydrocarbon system compounds, such as 1,7-octadien, 1,8-nonadiene, and 1,9-decadiene, Ether system compounds, such as O,O'-diarylbisphenol A and 3,3'-diarylbisphenol A, Carbonate system compounds, such as ester system compounds, such as diallyl phthalate, diallyl isophthalate, triallyl trimellitate, and tetraallyl pyromellitate, and diethylene-glycol diaryl carbonate, are mentioned.

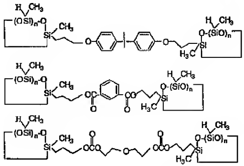
[0052]This compound can be obtained by dropping slowly an alkenyl group content compound mentioned to the bottom of existence of a hydrosilylation catalyst, and a top to an excessive amount of hydrosilyl group content compounds shown in the formulas 9-15. In consideration of compatibility to the acquisition ease of a raw material, the ease of carrying out of removal of a siloxane used superfluously, and also a polymer of the (A) ingredient, the following are preferred among such compounds.

[0053]

[Formula 5]



（nは2~4の整数、mは5~10の整数）



[0054]Although a polymer (A) and a hardening agent (B) are mixable at an arbitrary rate, it is preferred that the mole ratio of an alkenyl group and a hydrosilyl group is in the renga of 5-0.2 from the field of hardenability, and it is still more preferred that it is especially 2.5-0.4. If smaller [if a mole ratio becomes five or more, only a hardened material with insufficient hardening and small intensity with stickiness will be obtained, and] then 0.2, since a hydrosilyl group [activity / in a hardened material / after / hardening] remains in large quantities, a crack and a void occur, it will be uniform and a hardenad material with intensity will not be obtained.

[0055]Although a hardening reaction of a polymer (A) and a hardening agent (B) advances by mixing and heating two ingredients, a hydrosilylation catalyst is added in order to advance a reaction more nearly promptly. As such a hydrosilylation catalyst, radical initiators, such as organic peroxide and an azo compound, and a transition metal catalyst are mentioned. As a radical initiator, there is no restriction in particular and various kinds of things can be used. If it illustrates, di-t-butylperoxide, 2,5-dimethyl- 2,5-JI (t-butylperoxy) hexane, 2,5-dimethyl- 2,5-JI (t-butylperoxy)-3-hexyne, Dialkyl peroxide like dicumyl peroxide, t-butyl cumyl peroxide, alpha, and alpha'-bis(t-butylperoxy) isopropylbenzene, Benzoyl peroxide, p-chlorobenzoyl peroxide, m-chlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide, diacylperoxide like lauroyl peroxide, Peroxy-acid ester like perbenzoic acid-t-butyl, fault JI diisopropyl carbonate, Peroxyketal like peroxi dicarbonate like fault JI di-carbonate 2-ethylhexyl, 1,1-JI (t-butylperoxy) cyclohexane, and 1,1-JI (t-butylperoxy)-3,3,5-trimethylcyclohexane, etc. are mentioned.

[0056]As a transition metal catalyst, for example A platinum simple substance, alumina, silica, A complex with a thing which made carriers, such as carbon black, distribute a platinum solid, chloroplatinic acid, chloroplatinic acid, alcohol, aldehyde, ketone, etc., a platinum-olefin complex, and a platinum (0)-divinyl tetramethyl disiloxane complex are mentioned. As an example of catalysts other than a platinum compound, $RhCl(PPh_3)_3$, $RhCl_3$, $RuCl_3$, $IrCl_3$, $FeCl_3$, $AlCl_3$, $PdCl_2$-H_2O, $NiCl_2$, $TiCl_4$, etc. are mentioned. These catalysts may be used independently, and even if they use two or more kinds together, they are not cared about. Although there is no restriction in particular as a catalyst amount, it is good to use in the range of 10^{-3} - 10^{-6}mol to 1 mol of alkenyl groups of the (A) ingredient often [using in the range of 10^{-1} - 10^{-8}mol], and preferably. If less than 10^{-8}mol, hardening will not fully advance. Since a hydrosilylation catalyst is expensive, it is preferred that more than 10^{-1}mol does not use.

[0057]A uniform hardened material excellent in depthe hardenability is obtained without being accompanied by phenomena, such as foaming, if a hydrosilylation catalyst is mixed and stiffened [two ingredients (A), (B), and if needed]

for this invention. Although there is no restriction in particular about curing conditions, generally it is good to harden [0 ** - 200 **] at 30 ** - 150 ** preferably for 10 seconds - 24 hours. At an elevated temperature (80 ** - 150 **), what is hardened in a short time of 10 seconds - about 1 hour is obtained especially. Description of a hardened material can be broadly created from a rubber-like thing to a resin-like thing, although it is dependent on a principal chain skeleton and a molecular weight of a polymer of the (A) ingredient to be used, and a hardening agent of the (B) ingredient. If a concrete use of a hardened material obtained from this constituent is mentioned, they will be a sealing material, adhesives, an adhesive material, elastic adhesives, a paint, powder coatings, foam, a potting material for electric electrons, a film, a gasket, various molding materials, artificial marble, etc.

[0058]An acrylic polymer which has crosslinkable silyl groups at the end of this invention (meta), Like a manufacturing method of an acrylic polymer which has an alkenyl group at the end (meta), An organic halogenated compound or a sulfonyl halide compound An initiator, the 8th fellows of the periodic table, It can obtain by changing halogen of an acrylic polymer which has halogen (meta) into an end which is obtained by a polymerization method using a metal complex which uses nine fellows, ten fellows, or 11 group elements as a central metal as a catalyst and which shows by the general formula 1.

[0059]As such a converting method, an organic halogenated compound or a sulfonyl halide compound An initiator, An acrylic polymer which has terminal structures which show the 8th fellows of the periodic table, nine fellows, ten fellows, or 11 group elements in the general formula 1 with a polymerization method using a metal complex used as a central metal as a catalyst (meta) is manufactured, A method to which a compound having an alkenyl group and crosslinkable silyl groups of polymerization nature is made to react as the 2nd monomer is mentioned. This method is based on the same principle as a method illustrated in a manufacturing method of an acrylic polymer which has an alkenyl group at the end (meta). After the 1st polymerization ends the 2nd monomer and isolating a polymer also in this case, it may add with a catalyst and may be made to newly react, and it may add in the middle of a polymerization (inch-situ), and may be made to react. In the case of the latter, a monomer inversion rate of the 1st polymerization is so good that it is high, and is not less than 80% preferably. Crosslinkable silyl groups will be distributed over a side chain instead of a molecular terminal as it is 80% or less, and the mechanical characteristic of a hardened material will be spoiled. If a compound which has an alkenyl group and crosslinkable silyl groups of such polymerization nature is added in equivalent amount to the number of whole ends, crosslinkable silyl groups will be theoretically introduced into all the ends, but in order to introduce a cross-linking group into a whole end certainly, specifically, it is good to use one to 5 times to the number of ends in excessive amount. If it uses 5 or more times, a cross-linking group will be introduced into an end of a polymer by high density, and it is not desirable on hardened material physical properties.

[0060]Although there is no restriction in particular as a compound which combines and has such an alkenyl group and crosslinkable silyl groups of polymerization nature, if it illustrates concretely, general formula $6H_2C=C(R^3)-R^4-R^5-$ [Si $(R^{16})_{2-b}(Y)_bO]-_m-Si(R^{17})_{3-a}(Y)_a$ (6)

(R^3, R^4, and R^5 among a formula) R^3 in the general formula 2, R^4, and R^5 — the same — R^{16} and R^{17}, All An alkyl group of the carbon numbers 1-20, an aryl group, an aralkyl group, Or $(R')_3SiO$ - (R' is a univalent hydrocarbon group of the carbon numbers 1-20, and) three R' being the same and differing — **** — when the Tori ORGANO siloxy group shown is shown and R^{16} or two or more R^{17} exist, they may be the same and may differ. When Y shows a hydroxyl group or a hydrolytic basis and two or more Y exists, they may be the same and may differ. a shows 0, 1, 2, or 3, and b shows 0, 1, or 2. m is an integer of 0-19. However, it shall satisfy that it is a+mb>=1. A compound shown is mentioned. When R^4 is -C(O) O- (ester group), it is a compound of an acrylate (meta) system, and when R^4 is a phenylene group, it is a compound of a styrene system.

[0061]Especially as a hydrolytic basis shown by the above-mentioned Y, it is not limited, but can use a publicly known thing conventionally, and specifically, A point of hydrogen, a halogen atom, an alkoxy group, an acyloxy group, a KETOKISHI mate group, an amino group, an amide group, an acid-amide group, an aminooxy group, a sulfhydryl group, an alkenyloxy group, etc. being mentioned, and hydrolysis nature being mild and being easy to deal with it to especially an alkoxy group is preferred. This hydrolytic basis and a hydroxyl group can be combined with one silicon atom in the 1-3 ranges, and total of a+mb, i.e., a hydrolytic basis, has the preferred range of 1-5. When a hydrolytic basis and a hydroxyl group join together in [two or more] a reactive silicon group, they may be the same or may differ. The number of silicon atoms which constitute a cross-linking silicon compound may be one, and although they may be two or more pieces, in the case of a silicon atom connected by siloxane bond, there may be to about 20 pieces.

[0062]As an example of R^{16} in the general formula 6, or R^{17}, For example, aralkyl groups, such as aryl groups, such as cycloalkyl groups, such as alkyl groups, such as a methyl group and an ethyl group, and a cyclohexyl group, and a phenyl group, and benzyl, the Tori organosilyl group R' is indicated to be by $_3SiO-$ which is a methyl group, a phenyl group, etc. (R'), etc. are mentioned. Also in these, the reactivity of a hydrolytic silyl group is mild, and are easy to deal with it, and in that acquisition is easy, $H_2C=C(H)\,CO_2-(CH_2)_n-Si(OCH_3)_3$, $H_2C=C(H)\,CO_2-(CH_2)_n-Si(CH_3)(OCH_3)_2$, $H_2C=C(H)\,CO_2-(CH_2)_n-Si(OC_2H_5)_3$, $H_2C=C(H)\,CO_2-(CH_2)_n-Si(CH_3)(OC_2H_5)_2$, $H_2C=C(H)\,CO_2-(CH_2)_n-Si(OC_3H_7)_3$, $H_2C=C(H)\,CO_2-(CH_2)_n-Si(CH_3)(OC_3H_7)_2$, $H_2C=C(CH_3)\,CO_2-(CH_2)_n-Si(OCH_3)_3$, $H_2C=C(CH_3)\,CO_2-(CH_2)_n-Si(CH_3)(OCH_3)_2$, $H_2C=C(CH_3)\,CO_2-(CH_2)_n-Si(OC_2H_5)_3$, $H_2C=C(CH_3)\,CO_2-(CH_2)_n-Si(CH_3)(OC_2H_5)_2$, $H_2C=C(CH_3)\,CO_2-(CH_2)_n-Si(OC_3H_7)_3$, $H_2C=C(CH_3)\,CO_2-(CH_2)_n-Si(CH_3)(OC_3H_7)_2$ (the inside of each of above-mentioned formulas and n are the integers of 2-20),

$H_2C=C(H)\,CO_2-(CH_2)_n-O-(CH_2)_m-Si(OCH_3)_3$, $H_2C=C(H)\,CO_2-(CH_2)_n-O-(CH_2)_m-Si(CH_3)(OCH_3)_2$, $H_2C=C(H)\,CO_2-(CH_2)_n-O-(CH_2)_m-Si(OC_2H_5)_3$, $H_2C=C(H)\,CO_2-(CH_2)_n-O-(CH_2)_m-Si(CH_3)(OC_2H_5)_2$, $H_2C=C(H)\,CO_2-(CH_2)_n-O-(CH_2)_m-Si(OC_3H_7)_3$, $H_2C=C(H)\,CO_2-(CH_2)_n-O-(CH_2)_m-Si(CH_3)(OC_3H_7)_2$, $H_2C=C(CH_3)\,CO_2-(CH_2)_n-O-(CH_2)_m-Si(OCH_3)_3$, $H_2C=C(CH_3)\,CO_2-(CH_2)_n-O-(CH_2)_m-Si(CH_3)(OCH_3)_2$, $H_2C=C(CH_3)\,CO_2-(CH_2)_n-O-(CH_2)_m-Si(OC_2H_5)_3$, $H_2C=C(CH_3)\,CO_2-(CH_2)_n-O-(CH_2)_m-Si(CH_3)(OC_2H_5)_2$, $H_2C=C(CH_3)\,CO_2-(CH_2)_n-O-(CH_2)_m-Si(OC_3H_7)_3$, $H_2C=C(CH_3)\,CO_2-(CH_2)_n-O-(CH_2)_m-Si(CH_3)(OC_3H_7)_2$ (as for the inside of each of above-mentioned formulas, and n, an integer of 1-20 and m are the integers of 2-20),

o-, m-, p-$H_2C=CH-C_6H_4-(CH_2)_n-Si(OCH_3)_3$, o-, m-, p-$H_2C=CH-C_6H_4-(CH_2)_n-Si(CH_3)(OCH_3)_2$, o-, m-, p-$H_2C=CH-C_6H_4-O-(CH_2)_n-Si(OCH_3)_3$, o-, m-, p-$H_2C=CH-C_6H_4-O-(CH_2)_n-Si(CH_3)(OCH_3)_2$ (however, inside of above-mentioned chemical formula, and C_6H_4 a phenylene group and n integer of 2-20.)

** -- it is desirable.

[0063]In a manufacturing method of an acrylic polymer using a metal complex which uses an initiator, the 8th fellows of the periodic table, nine fellows, ten fellows, or 11 group elements as a central metal for an organic halogenated compound or a sulfonyl halide compound as a catalyst (meta), If an organic halogenated compound which has crosslinkable silyl groups is used as an initiator, an acrylic polymer which has crosslinkable silyl groups in one end and in which other ends have the structure of the formula 1 (meta) will be obtained. Thus, if halogen of a stop end of a polymer obtained is changed into a crosslinkable-silyl-groups content substituent, an acrylic polymer which has crosslinkable silyl groups in both ends (meta) can be obtained. An already indicated method can be used as the converting method.

[0064]Although there is no restriction in particular as an organic halogenated compound which has crosslinkable silyl

groups, what has the structure shown, for example in the general formula 7 is illustrated.

$R^{11}R^{12}C(X)-R^{13}-R^{14}-C(H)(R^1)\,CH_2-[Si(R^{16})_{2-b}(Y)_bO]_m-Si(R^{17})_{3-a}(Y)_a$ (7)

(The inside of a formula, R^1, R^{11}, R^{12}, R^{13}, R^{14}, R^{16}, R^{17}, a, b, m, X, and Y are the same as the above)

If a compound of the formula 7 is illustrated concretely, $XCH_2C(O)\,O(CH_2)_nSi(OCH_3)_3$, $CH_3C(H)(X)C(O)\,O(CH_2)_nSi(OCH_3)_3$, $(CH_3)_2C(X)C(O)\,O(CH_2)_nSi(OCH_3)_3$, $XCH_2C(O)\,O(CH_2)_nSi(CH_3)(OCH_3)_2$, $CH_3C(H)(X)C(O)\,O(CH_2)_nSi(CH_3)(OCH_3)_2$, $(CH_3)_2C(X)C(O)\,O(CH_2)_nSi(CH_3)(OCH_3)_2$ (in each of above-mentioned formulas, as for X, chlorine, bromine, iodine, and n are the integers of 0-20),

$XCH_2C(O)\,O(CH_2)_nO(CH_2)_mSi(OCH_3)_3$, $H_3CC(H)(X)C(O)\,O(CH_2)_nO(CH_2)_mSi(OCH_3)_3$, $(H_3C)_2C(X)C(O)\,O(CH_2)_nO(CH_2)_mSi(OCH_3)_3$, $CH_3CH_2C(H)(X)C(O)\,O(CH_2)_nO(CH_2)_mSi(OCH_3)_3$, $XCH_2C(O)\,O(CH_2)_nO(CH_2)_mSi(CH_3)(OCH_3)_2$, $H_3CC(H)(X)C(O)\,O(CH_2)_nO(CH_2)_m-Si(CH_3)(OCH_3)_2$, $(H_3C)_2C(X)C(O)\,O(CH_2)_nO(CH_2)_m-Si(CH_3)(OCH_3)_2$, $CH_3CH_2C(H)(X)C(O)\,O(CH_2)_nO(CH_2)_m-Si(CH_3)(OCH_3)_2$ (as for chlorine, bromine, iodine, and n, in X, in each of above-mentioned formulas, an integer of 1-20 and m are the integers of 0-20),

o,m,p-$XCH_2-C_6H_4-(CH_2)_2Si(OCH_3)_3$, o,m,p-$CH_3C(H)(X)-C_6H_4-(CH_2)_2Si(OCH_3)_3$, o,m,p-$CH_3CH_2C(H)(X)-C_6H_4-(CH_2)_2Si(OCH_3)_3$, o,m,p-$XCH_2-C_6H_4-(CH_2)_3Si(OCH_3)_3$, o,m,p-$CH_3C(H)(X)-C_6H_4-(CH_2)_3Si(OCH_3)_3$, o,m,p-$CH_3CH_2C(H)(X)-C_6H_4-(CH_2)_3Si(OCH_3)_3$, o,m,p-$XCH_2-C_6H_4-(CH_2)_2-O-(CH_2)_3Si(OCH_3)_3$, o,m,p-$CH_3C(H)(X)-C_6H_4-(CH_2)_2-O-(CH_2)_3Si(OCH_3)_3$, o,m,p-$CH_3CH_2C(H)(X)-C_6H_4-(CH_2)_2-O-(CH_2)_3Si(OCH_3)_3$, o,m,p-$XCH_2-C_6H_4-O-(CH_2)_3Si(OCH_3)_3$, o,m,p-$CH_3C(H)(X)-C_6H_4-O-(CH_2)_3Si(OCH_3)_3$, o,m,p-$CH_3CH_2C(H)(X)-C_6H_4-O-(CH_2)_3-Si(OCH_3)_3$, o,m,p-$XCH_2-C_6H_4-O-(CH_2)_2-O-(CH_2)_3-Si(OCH_3)_3$, o,m,p-$CH_3C(H)(X)-C_6H_4-O-(CH_2)_2-O-(CH_2)_3Si(OCH_3)_3$, O,m,p-$CH_3CH_2C(H)(X)-C_6H_4-O-(CH_2)_2-O-(CH_2)_3Si(OCH_3)_3$ (in each of above-mentioned formulas, X is chlorine, bromine, or iodine),

** is mentioned.

[0065]What has further the structure shown by the general formula 8 as an organic halogenated compound which has crosslinkable silyl groups is illustrated.

$(R^{17})_{3-a}(Y)_aSi-[OSi(R^{16})_{2-b}(Y)_b]_m-CH_2-C(H)(R^1)-R^{14}-C(R^{11})(X)-R^{15}-R^{12}$ (8)

(The inside of a formula, R^1, R^{11}, R^{12}, R^{14}, R^{15}, R^{16}, R^{17}, a, b, m, X, and Y are the same as the above)

If such a compound is illustrated concretely, $(CH_3O)_3SiCH_2CH_2C(H)(X)C_6H_5$, $(CH_3O)_2(CH_3)SiCH_2CH_2C(H)(X)C_6H_5$, $(CH_3O)_3Si(CH_2)_2C(H)(X)-CO_2R$, $(CH_3O)_2(CH_3)Si(CH_2)_2C(H)(X)-CO_2R$, $(CH_3O)_3Si(CH_2)_3C(H)(X)-CO_2R$, $(CH_3O)_2(CH_3)Si(CH_2)_3C(H)(X)-CO_2R$, $(CH_3O)_3Si(CH_2)_4C(H)(X)-CO_2R$, $(CH_3O)_2(CH_3)Si(CH_2)_4C(H)(X)-CO_2R$, $(CH_3O)_3Si(CH_2)_9C(H)(X)-CO_2R$, $(CH_3O)2(CH_3)Si(CH_2)_9C(H)(X)-CO_2R$, $(CH_3O)3Si(CH_2)_3C(H)(X)-C_6H_5$, $(CH_3O)_2(CH_3)Si(CH_2)_3C(H)(X)-C_6H_5$, $(CH_3O)_3Si(CH_2)_4C(H)(X)-C_6H_5$, $(CH_3O)2(CH_3)Si(CH_2)_4C(H)(X)-C_6H_5$ (in each of above-mentioned formulas), As for X, chlorine, bromine or iodine, and R are an alkyl group of the carbon numbers 1-20, an aryl group, and an aralkyl group.

** is mentioned.

[0066]If an organic halogenated compound which has crosslinkable silyl groups is used as an initiator, a polymer which is a halogen end where one end is shown by crosslinkable silyl groups and other ends are shown by the formula 1 will be obtained, but. An acrylic polymer which has crosslinkable silyl groups at the end (meta) can be obtained also by carrying

out coupling of the halogen ends using a compound which can replace halogen of the formula 1 of this polymer and which has a total of two or more same or different functional groups. All compounds that have two or more functional groups which can replace halogen of the formula 1 which is based on the same principle as a method explained in a manufacturing method of an acrylic polymer which has an alkenyl group at the end (meta), and was already illustrated can be used for this method.

[0067]In addition to this as a manufacturing method of an acrylic polymer which has crosslinkable silyl groups at the end (meta), a method to which a hydrosilane compound which has a cross-linking group is made to add is mentioned to an acrylic polymer which has an alkenyl group at the end (meta). As an acrylic polymer which has an alkenyl group at the end (meta), all things obtained by an already explained method can be used conveniently.

[0068]although there is no restriction in particular as a hydrosilane compound, if a typical thing is shown — general formula 16H- $[Si(R^{16})_{2-b}(Y)_bO]_m-Si(R^{17})_{3-a}(Y)_a$ (16)

(R^{16}, R^{17}, Y, a, and b are the same as them in the general formula 6 among a formula.) — a compound expressed is illustrated.

[0069]As an example of a hydrolytic basis shown by the above-mentioned Y and R^{16}, and R^{17}, what was already illustrated by explanation of the general formula 6, and same thing are mentioned. Also in these hydrosilane compound, it is general formula 17 H-$Si(R^{17})_{3-a}(Y)_a$ (17) especially.

(R^{17}, Y, and a are the same as the above among a formula.) — a hydrosilane compound which has a cross-linking group with which it is expressed — acquisition — it is desirable from an easy point. As an example of a hydrosilane compound of having a cross-linking group shown by the general formula 16 or 17, $HSiCl_3$, $HSi(CH_3)Cl_2$, and $HSi(CH_3)_2Cl$, $HSi(OCH_3)_3$, $HSi(CH_3)(OCH_3)_2$, $HSi(CH_3)_2OCH_3$, $HSi(OC_2H_5)_3$, $HSi(CH_3)(OC_2H_5)_2$, $HSi(CH_3)_2OC_2H_5$, $HSi(OC_3H_7)_3$, $HSi(C_2H_5)(OCH_3)_2$, $HSi(C_2H_5)_2OCH_3$, $HSi(C_6H_5)(OCH_3)_2$, $HSi(C_6H_5)_2(OCH_3)$, $HSi(CH_3)(OC(O)CH_3)_2$, $HSi(CH_3)_2O-[Si(CH_3)_2O]_2-Si(CH_3)(OCH_3)_2$, $HSi(CH_3)[O-N=C(CH_3)_2]_2$ (however, C_6H_5 shows a phenyl group among the above-mentioned chemical formula)

** is mentioned.

[0070]When making a hydrosilane compound which has such crosslinkable silyl groups add to an acrylic polymer which has an alkenyl group at the end (meta), a hydrosilylation catalyst is used and all already described things can be used. The acrylic polymer which was produced by performing it above and which has crosslinkable silyl groups at the end (meta) can make this a hardenability constituent used as the main ingredients.

[0071]An acrylic polymer which is the main ingredients (meta) may be used independently, or two or more kinds may be mixed and it may be used. Although there is no restriction in particular about the molecular weight, it is preferred that it is in the range of 500-50000. The original characteristic of an acrylic (meta) polymer is it hard to be revealed that a molecular weight is 500 or less, and handling becomes it difficult that it is 50000 or more.

[0072]If an acrylic polymer which has a hydrolytic silyl group at the end (meta) contacts moisture, it will three-dimension-ize by crosslinking reaction, and it will be hardened. Since a hydrolysis rate changes with the kinds of temperature, humidity, and hydrolytic basis, it must choose a suitable hydrolytic basis according to a service condition. The acrylic polymer which has a hydrolytic silyl group at the end (meta) needs to sever contact with moisture as much as possible at the time of preservation.

[0073]A curing catalyst may be added in order to promote a hardening reaction. As a catalyst, amine salt, such as an alkyl titanate, an organic silicon titanate, tin octylate and metal salt of carboxylic acid like dibutyltin dilaurate, and dibutyl amine 2-ethylhexoate, other acid catalysts, and a basic catalyst can be used. Although there is no restriction in particular as the amount used, it is preferred to use for an end 0.01 to 5% of the weight to an acrylic polymer which has crosslinkable silyl

groups (meta).

[0074]If an end which is the main ingredients is made to mix and harden a condensation catalyst to an acrylic polymer which has crosslinkable silyl groups (meta) if needed, a uniform hardened material can be obtained. Although there is no restriction in particular as curing conditions, generally 0-100 ** is 1 hour - about one week at 10-50 ** preferably. Description of a hardened material can be broadly created from a rubber-like thing to a resin-like thing, although it is dependent on a principal chain skeleton and a molecular weight of a polymer to be used.

[0075]If a concrete use of a hardened material obtained from the above-mentioned constituent is mentioned, they will be a sealing material, adhesives, an adhesive material, elastic adhesives, a paint, powder coatings, foam, a potting material for electric electrons, a film, a molding material, artificial marble, etc.

[0076]

[Example]Although the concrete example of this invention is shown below, this invention is not limited to the following example.

[0077]

[The example 1 of manufacture]

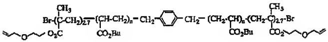
(Composition of 2-allyloxy ethyl methacrylate) An agitator, a thermometer, a flowing-back condenser tube, To the three-neck flask furnished with the Dean Stark pipe, it is methacrylic acid (137.7 g), 1.6 mol, ethylene glycol monoallyl ether (60.7 g, 0.6 mol), p-toluenesulfonic acid (0.76 g, 4.0mmol), and toluene (650mL) were taught. After making it react at 120 ** for 5 hours, 0.12g of p-toluenesulfonic acid was added, it was made to react at the still more nearly same temperature for 6 hours, and 0.1g of p-toluenesulfonic acid was added. It was made to react at the same temperature for further 9 hours, and the reaction was ended. In the meantime, methacrylic acid and ethylene glycol monoallyl ether were pursued with liquid chromatography, and the inversion rate reached to 98% eventually. $NaHCO_3$ solution was added, and it neutralized and separated two-layer. The water layer was extracted once with toluene, and after drying an organic layer by $CaCl_2$, volatile matter content was distilled off under decompression. By what is done for the distillation under reduced pressure of the rough product (60 **, 2mmHg), 98.7g of 2-allyloxy ethyl methacrylate shown in a lower type was obtained (73% of yield).

$H_2C=C(CH_3)CO_2(CH_2)_2OCH_2CH=CH_2$[0078]

[Work example 1]To the resisting pressure glass reaction vessel of 30mL, it is butyl acrylate (2.5 mL), 2.24-g, 17.45mmol, alpha, and alpha'-dibromo-p-xylene (92.5 mg) 0.35mmol, the first copper (50 mg, 0.35mmol) of bromination, a 2,2'-bipyridyl (163 mg, 1.05mmol) and ethyl acetate (2mL), and acetonitrile (0.5mL) were taught, and the sealed tube was carried out, after blowing nitrogen gas for 10 minutes and removing dissolved oxygen. The mixture was heated at 130 ** and made to react for 1 hour. After cooling to a room temperature, the sealed tube of the allyloxy ethyl methacrylate (600 mg, 3.5mmol) obtained in the example 1 of manufacture was added and carried out under a nitrogen gas atmosphere. The mixture was heated at 60 ** and made to react for 1 hour. After diluting the mixture with ethyl acetate (20mL) and filtering the generated insoluble solid, dilute hydrochloric acid washed filtrate once by brine twice. The organic layer was dried by Na_2SO_4, volatile matter content was distilled off under decompression, and 1.97g of polybutyl acrylate which has an alkenyl group in the both ends shown in a lower type was obtained (86% of polymerization yield). By GPC measurement (polystyrene conversion), the number average molecular weight of the polymer was 6700, and molecular weight distribution was 1.60. The number of the alkenyl groups introduced per one molecule of oligomer was 5.4 from ^{1}HNMR analysis.

[0079]

[Formula 6]

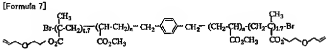


[0080]

[Work example 2]In Example 1, the poly(methyl acrylate) which completely has an alkenyl group in a similar manner in the both ends which have the structure of a lower type was obtained except using methyl acrylate instead of butyl acrylate (93% of yield). In GPC measurement, by (polystyrene conversion), the number average molecular weight of the polymer was 7900, and molecular weight distribution was 2.0. The number of the alkenyl groups introduced per one molecule of oligomer was an average of 3.3 from ^{1}H NMR analysis.

[0081]

[Formula 7]



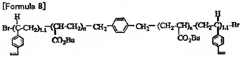
[0082]

[Work example 3]To the resisting pressure glass reaction vessel of 50mL, it is butyl acrylate (8.94 g 10 mL). 69.8mmol, alpha, and alpha'-dibromo-p-xylene (370 mg) 1.4mmol, the first copper (200 mg, 1.4mmol) of bromination, a 2,2'-bipyridyl (433 mg, 2.8mmol), and methyl isobutyl ketone (10mL) were taught, and the sealed tube was carried out, after blowing nitrogen gas for 10 minutes and removing dissolved oxygen. The mixture was heated at 130 ** and made to react for 20 minutes. After filtering the insoluble solid which diluted the mixture with ethyl acetate (20mL), and generated it after cooling to a room temperature, dilute hydrochloric acid washed filtrate once by brine twice. The organic layer was dried by Na_2SO_4, volatile matter content was distilled off under decompression, and 5.21g of poly (butyl acrylate) which has bromine in both ends was obtained (58%). By GPC measurement (polystyrene conversion), the number average molecular weight of the polymer was 3700, and molecular weight distribution was 1.41.

[0083]Next, the poly (butyl acrylate) (2.0g) produced by the resisting pressure coll of 30mL by performing it above, p-divinylbenzene (281 mg, 2.16mmol), the first copper of bromination (77 mg) 0.54mmol, a 2,2'-bipyridyl (167 mg, 1.08mmol), and methyl isobutyl ketone (4mL) were taught, and the sealed tube was carried out, after blowing nitrogen gas for 10 minutes and removing dissolved oxygen. The mixture was heated at 130 ** and made to react for 30 minutes. After filtering the insoluble solid which diluted the mixture with ethyl acetate (10mL), and generated it after cooling to a room temperature, dilute hydrochloric acid washed filtrate once by brine twice. The organic layer was dried by Na_2SO_4, volatile matter content was distilled off under decompression, and 2.11g of poly (butyl acrylate) which has an alkanyl group in the both ends shown in a lower type was obtained. By GPC measurement (polystyrene conversion), the number average molecular weight of the polymer was 7300, and molecular weight distribution was 2.47. The number of the alkenyl groups introduced per one molecula of oligomer was 2.1 from ^{1}H NMR analysis.

[0084]

[Formula 8]



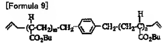
[0085]

[Work example 4]To the resisting pressure glass reaction vessel of 30mL, it is butyl acrylate (4.47 g 5 mL). 34.9mmol,

alpha, and alpha'-dibromo-p-xylene (180 mg) 0.69mmol, the first copper (98 mg, 0.69mmol) of bromination, a 2,2'-bipyridyl (319 g, 2.06mmol) and ethyl acetate (4mL), and acetonitrile (1 ml) were taught, and the sealed tube was carried out, after blowing nitrogen gas for 10 minutes and removing dissolved oxygen. The mixture was heated at 130 ** and made to react for 1 hour. Allyl tributyl tin (0.51mL, 1.64mmol) was added under a nitrogen atmosphere after cooling a mixture, and it was made to react at 100 ** for 1 hour. After diluting the mixture with ethyl acetate (20mL) and filtering the generated insoluble solid, dilute hydrochloric acid washed filtrate once by brine twice. The organic layer was dried by Na_2SO_4, volatile matter content was distilled off under decompression, and the mixture of the polybutyl acrylate which has an alkenyl group in the both ends shown in a lower type, and bromo tributyl tin was obtained (yield of 4.48g). In GPC measurement, by (polystyrene conversion), the number average molecular weight of the polymer was 7700, and molecular weight distribution was 1.33. The number of the alkenyl groups introduced per one molecule of oligomer was 1.6 from ^{1}H NMR analysis.

[0086]

[Formula 9]

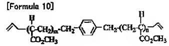


[0087]

[Work example 5]To the resisting pressure glass reactor of 30mL, it is methyl acrylate (4.78 g 5 mL). 55.6mmol, alpha, and alpha'-dibromo-p-xylene (292 mg) 1.11mmol, the first copper (159 mg, 1.11mmol) of bromination, a 2,2'-bipyridyl (518 mg, 3.3mmol) and ethyl acetate (4mL), and acetonitrile (1mL) were taught, and the sealed tube was carried out, after performing vacuum devolatilization twice and removing dissolved oxygen. The mixture was heated at 130 ** and made to react for 2.7 hours. After cooling to a room temperature, allyl tributyl tin (0.82mL, 2.66mmol) was added, and it was made to react at 80 ** for 6 hours. After diluting the mixture with ethyl acetate (20mL) and filtering the generated insoluble solid, dilute hydrochloric acid washed filtrate once by brine twice. The organic layer was dried by Na_2SO_4, and volatile matter content was distilled off under decompression. The rough product was melted in a small amount of acetone, it reprecipitated twice by hexane, and the poly(methyl acrylate) which has an alkanyl group in the both ends shown in a lower type was obtained (yield of 2.80g). In GPC measurement, by (polystyrene conversion), the number average molecular weight of the polymer was 7000, and molecular weight distribution was 1.26. The number of the alkenyl groups introduced per one molecule of oligomer was 1.7 from ^{1}H NMR analysis.

[0088]

[Formula 10]



[0089]

[The example 2 of manufacture]

(Manufacture 1 of the organic halogenated compound which has an alkenyl group) The nitrogen purge of the two-lot flask of 50mL was carried out, and 2-allyloxy ethanol (2.5mL, 23.4mmol), pyridine (3mL), and THF (10mL) were taught. The solution was cooled at 0 ** and 2-bromo propionyl chloride (2mL, 19.52mmol) was dropped slowly. After continuing churning at a temperature as it is for 1 hour, filtration removed the hydrochloride of the pyridine which added and generated ethyl acetate (10mL). filtrate -- dilute hydrochloric acid (10mL) and $NaHCO_3$ solution (10mL) -- it washed by

brine (10mL) further. The organic layer was dried by Na_2SO_4, and volatile matter content was decompression—ization-distilled off. By carrying out distillation under reduced pressure of the obtained rough product, the allyloxy ethyl-2-bromo propionate shown in a lower type was obtained. (78.5-81 ** (1.3mmHg), 2.986g).

[0090]$CH_3C(H)(Br)C(O)O-CH_2CH_2-O-CH_2CH=CH_2$[0091]

[The example 3 of manufacture]

(Manufacture 2 of the organic halogenated compound which has an alkenyl group) The nitrogen purge of the two-lot flask of 50mL was carried out, and a 5-hexen-1-oar (2.81mL, 23.4mmol), pyridine (3mL), and THF (10mL) were taught. The solution was cooled at 0 ** and 2-bromo propionyl chloride (2mL, 19.52mmol) was dropped slowly. After continuing churning at a temperature as it is for 1 hour, filtration removed the hydrochloride of the pyridine which added and generated ethyl acetate (10mL), filtrate — dilute hydrochloric acid (10mL) and $NaHCO_3$ solution (10mL) — it washed by brine (10mL) further. The organic layer was dried by Na_2SO_4, and volatile matter content was decompression—ization-distilled off. By carrying out distillation under reduced pressure of the obtained rough product, the hexenyl-2-bromo propionate shown in a lower type was obtained. (82-83 ** (2.3mmHg), 3.101g).

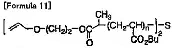
$CH_3C(H)(Br)C(O)O-(CH_2)_4-CH=CH_2$[0092]

[Work example 6]To the resisting pressure glass reaction vessel of 30mL, it is butyl acrylate (2.5 mL). The initiator which has the alkenyl group obtained in 2.24 g, 17.45mmol, and the example 2 of manufacture (165 mg) 0.698mmol, the first copper (100 mg, 0.698mmol) of bromination, a 2,2'-bipyridyl (218 mg, 1.40mmol), acetonitrile (0.5mL), and ethyl acetate (2mL) were prepared, and the sealed tube was carried out, after blowing nitrogen gas for 10 minutes and removing dissolved oxygen. The mixture was heated at 130 ** and made to react for 50 minutes. After filtering the insoluble solid which diluted the mixture with ethyl acetate (20mL), and generated it after cooling to a room temperature, dilute hydrochloric acid washed filtrate once by brine twice. The organic layer was dried by Na_2SO_4, volatile matter content was distilled off under decompression, and 1.90g of poly (butyl acrylate) which has bromine was obtained in an alkenyl group and other ends to one end (79%). In GPC measurement, by (polystyrene conversion), the number average molecular weight of the polymer was 3600, and molecular weight distribution was 1.51. The number of the alkenyl groups introduced per one molecule of oligomer was 0.75 from ^1H NMR analysis.

[0093]Next, the polymer (1.90g) produced by 3 mouth flask of 50mL provided with the stirring bar and the flowing-back condenser tube by performing it above, $Na_2S.9H_2O$ (70.2 mg, 0.293mmol), and ethanol (3mL) were taught, and it agitated at flowing-back temperature for 3 hours. After cooling to a room temperature, ethyl acetate (10mL) and dilute hydrochloric acid (10mL) were added, and it separated two-layer. After washing the organic layer by dilute hydrochloric acid and brine and drying by Na_2SO_4, 1.69g of poly(acrylic acid) butyl which has an alkenyl group in the both ends shown in a lower type was obtained by distilling off volatile matter content under decompression. In GPC measurement, by (polystyrene conversion), the number average molecular weight of the polymer was 5100, and molecular weight distribution was 1.73.

[0094]

[Formula 11]



[0095]

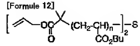
[Work example 7]To the resisting pressure glass reaction vessel of 30mL, it is methyl acrylate (4.78 g 5 mL), 55.5mmol, 2-

methyl-2-bromopropionic acid allyl (0.354 mL) 460 mg, 2.22mmol, the first copper (318 mg, 2.22mmolmmol) of bromination, a 2,2'-bipyridyl (1.04 g, 6.66mmol), acetonitrile (1mL), and ethyl acetate (4mL) were prepared, and the sealed tube was carried out, after performing the vacuum deairing 3 times and removing dissolved oxygen. The mixture was heated at 80 ** and made to react for 3 hours. After filtering the insoluble solid which diluted the mixture with ethyl acetate (20mL), and generated it after cooling to a room temperature, dilute hydrochloric acid washed filtrate once by brine twice. The organic layer was dried by Na_2SO_4, volatile matter content was distilled off under decompression, and 3.93g of poly (butyl acrylate) which has bromine was obtained in an alkenyl group and other ends to one end (75%). By GPC measurement (polystyrene conversion), the number average molecular weight of the polymer was 2700, and molecular weight distribution was 1.48. The number of the alkenyl groups introduced per one molecule of oligomer was 0.81 from ^1H NMR analysis.

[0096]Next, the polymer (1.17g) produced by 3 mouth flask of 50mL provided with the stirring bar and the flowing-back condenser tube by performing it above, $Na_2S.9H_2O$ (57.6 mg, 0.240mmol), and ethanol (2mL) were taught, and it agitated at flowing-back temperature for 3 hours. After cooling to a room temperature, ethyl acetate (10mL) and dilute hydrochloric acid (10mL) were added, and it separated two-layer. After washing the organic layer by dilute hydrochloric acid and brine and drying by Na_2SO_4, 1.11g of poly(acrylic acid) butyl which has an alkenyl group in the both ends shown in a lower type was obtained by distilling off volatile matter content under decompression. In GPC measurement, by (polystyrene conversion), the number average molecular weight of the polymer was 4200, and molecular weight distribution was 1.71.

[0097]

[Formula 12]

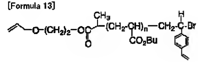


[0098]

[Work example 8]To the resisting pressure glass reaction vessel of 100mL, it is butyl acrylate (10 mL). The initiator which has the alkenyl group obtained in 8.94 g, 69.8mmol, and the example 2 of manufacture (332 mg) 1.40mmol, the first copper (200 mg, 1.40mmol) of bromination, a 2,2'-bipyridyl (433 mg, 2.80mmol), acetonitrile (2mL), and ethyl acetate (8mL) were prepared, and the sealed tube was carried out, after blowing nitrogen gas for 10 minutes and removing dissolved oxygen. The mixture was heated at 130 ** and made to react for 1.5 hours. After cooling to a room temperature, the sealed tube of the p-divinylbenzene (364 mg, 2.80mmol) was added and carried out under a nitrogen gas atmosphere. The mixture was heated at 100 ** and made to react for 2 hours. After diluting the mixture with ethyl acetate (30mL) and filtering the generated insoluble solid, dilute hydrochloric acid washed filtrate once by brine twice. The organic layer was dried by Na_2SO_4, volatile matter content was distilled off under decompression, and 6.43g of polybutyl acrylate which has an alkenyl group in the both ends shown in a lower type was obtained (69%). By GPC measurement (polystyrene conversion), the number average molecular weight of the polymer was 3900, and molecular weight distribution was 5.35. The number of the alkenyl groups introduced per one molecule of oligomer was 1.73 from ^1H NMR analysis.

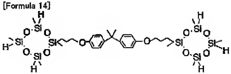
[0099]

[Formula 13]



[0100]
[Examples 9-14] The polymer which has an alkenyl group in the both ends obtained in creation examples 1, 2, 3, 6, 7, and 8 of the hardened material was dissolved in toluene, and a polymer and equivalent weight of silicic acid aluminum (the product made from harmony chemicals: KYO word 700PEL) were added. It agitated for 1 hour, and the minute impurities in a polymer were removed. Next, 1, 1 and 3 of the multivalent hydrogen silicon compound shown in a lower type and zerovalent platinum, 3-tetramethyl 1, and 3-divinyl disiloxane complex (8.3×10^{-8}mol/L xylene solution) were well mixed with the refined poly (acrylic ester). The quantity from which, as for the amount of the multivalent hydrogen silicon compound used, the alkenyl group of a polymer and the hydrosilyl group of a hydrogen silicon compound will be 1/1.2 by a mole ratio, and the amount of the platinum catalyst used were made into the 10^{-4} - 10^{-3} equivalent by the mole ratio to the alkenyl group of a polymer.

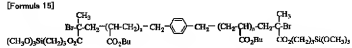
[0101]Thus, the hardening examination was done on a 130 ** hot plate for some obtained constituents, and gel time was measured. It deaerated under decompression of the remaining constituents, heat cura was slushed and carried out to the mold, and the rubber-like hardened material was obtained. The hardened material was immersed in toluene for 24 hours, and the gel fraction was measured from weight changes in front and behind. The result was shown in Table 1.

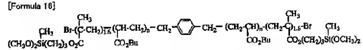
[0102]
[Formula 14]


[0103]
[Table 1]

実施例	重合体	白金触媒の使用量（モル%）	130℃におけるゲル化時間	硬化物作成条件	硬化物のゲル分率（%）
実施例9	実施例1の重合体	10^{-4}	3分	100℃ 15時間	81
実施例10	実施例2の重合体	10^{-4}	45秒	100℃ 17時間	55
実施例11	実施例3の重合体	10^{-3}	1分40秒	100℃ 3時間	77
実施例12	実施例6の重合体	10^{-3}	4分	100℃ 18時間	77
実施例13	実施例7の重合体	10^{-3}	2分	100℃ 15時間	40
実施例14	実施例8の重合体	10^{-3}	11秒	100℃ 12時間	84

[0104]
[Work example 15]To the resisting pressure glass reaction vessel of 30mL, it is butyl acrylate (4.47 g 5 mL) 34.9mmol, alpha, and alpha'-dibromo-p-xylene (185 mg) 0.70mmol, the first copper (100 mg, 0.70mmol) of bromination, a 2,2'-bipyridyl (1.09 g, 7.0mmol), and acetonitrile (5mL) were taught, and the sealed tube was carried out, after performing vacuum devolatilization 3 times and removing dissolved oxygen. The mixture was heated at 130 ** and made to react for 6 hours. After diluting the mixture with ethyl acetate (mL) and filtering the generated insoluble solid, dilute hydrochloric acid washed filtrate once by brine 3 times. The organic layer was dried by Na_2SO_4, volatile matter content was distilled off under decompression, and the poly (butyl acrylate) which has bromine in both ends was obtained (3.04 g, 68% of

polymerization yield). By GPC measurement (polystyrene conversion), the number average molecular weight of the polymer was 5200, and molecular weight distribution was 1.17. Next, the poly (butyl acrylate) (1g) which has bromine in the both ends obtained by the resisting pressure coil of 30mL in the top, Trimethoxysilylpropyl methacrylate (285 mg, 1.15mmol), When copper (27.6 mg, 0.193mmol), a 2,2'-bipyridyl (300 mg, 1.93mmol), and ethyl acetate (3mL) were prepared for a start [bromination] and it was made to react at 130 ** for 6 hours, the poly (butyl acrylate) which has a trimethoxysilyl group at the end shown in a lower type was obtained.
[0105]
[Formula 15]


[0106]
[Work example 16]To the resisting pressure glass reaction vessel of 30mL, it is butyl acrylate (4.47 g 5 mL) 34.9mmol, alpha, and alpha'-dibromo-p-xylene (185 mg) 0.70mmol, the first copper (100 mg, 0.70mmol) of bromination, a 2,2'-bipyridyl (217 mg, 1.40mmol), ethyl acetate (4mL), and acetonitrile (1mL) were taught, and the sealed tube was carried out, after performing nitrogen bubbling for 10 minutes and removing dissolved oxygen. The mixture was heated at 130 ** and made to react for 2 hours. After cooling a mixture, methyl dimethoxy silyl propyl methacrylate (650 mg, 2.8mmol) was added, and it was made to react at 100 ** for 2 hours. After diluting with ethyl acetate (20mL) after cooling a mixture and filtering the generated insoluble solid, ammonium chloride solution washed filtrate once by brine twice. The organic layer was dried by Na_2SO_4, volatile matter content was distilled off under decompression, and 4.78g of poly (butyl acrylate) which has a methyl dimethoxy silyl group in the both ends shown in a lower type was obtained (90%). By GPC measurement (polystyrene conversion), the number average molecular weight of the polymer was 7100, and molecular weight distribution was 1.74. The number of the silyl groups introduced per monad by ^{1}HNMR analysis was 3.2.
[0107]
[Formula 16]


[0108]Next, poly (butyl acrylate) (2.5g) and the curing catalyst (Japanese East transformation make, U-220 or 75 mg) which have crosslinkable silyl groups in the both ends produced by performing it above were mixed well, and it slushed into the mold, and defoamed at the room temperature using decompression oven. The uniform rubber-like hardened material was obtained by neglecting it for seven days to a room temperature. The gel fraction was 54%.
[0109]
[Effect of the Invention]In this invention, the acrylic (meta) polymer in which manufacturing until now has an alkenyl group or a hydrolytic silyl group by a high ratio at the difficult end can be obtained simple, and those functional groups are certainly introduced into the end.
Therefore, the hardened material which was excellent in the hardening characteristic can be obtained.

[Translation done.]